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14. ABSTRACT A recently developed sub-class of POSS, fluorinated polyhedral oligomeric silsesquioxane (F-POSS), consists of a Si-O core with a periphery of fluorinated chains ranging from 6-12 carbon atoms in length. These structures possess some of the lowest surface energies for any known crystalline solid. This sub-class has been based on completely-condensed silsesquioxane cages with no means of chemical functionalization. Herein, an incompletely-condensed silsesquioxane, (CF ₃ (CF ₂) ₇ CH ₂ CH ₂) ₈ Si ₈ O ₁₁ (OH) ₂ , has been synthesized via a multi-step synthesis (52% yield). The structure was confirmed with ²⁹ Si NMR, elemental analysis, and X-ray diffraction. X-ray diffraction revealed an incompletely-condensed structure that contains inter- and intramolecular hydrogen bonding between silanols. This structure is currently being functionalized to produce a wide variety of functional F-POSS based compounds and polymers.					
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INCOMPLETELY-CONDENSED FLUORINATED SILSESQUIOXANE: SYNTHESIS AND CRYSTAL STRUCTURE

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A recently developed sub-class of POSS, fluorinated polyhedral oligomeric silsesquioxane (F-POSS), consists of a Si-O core with a periphery of fluorinated chains ranging from 6-12 carbon atoms in length. These structures possess some of the lowest surface energies for any known crystalline solid. This sub-class has been based on completely-condensed silsesquioxane cages with no means of chemical functionalization. Herein, an incompletely-condensed silsesquioxane, $(\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2)_8\text{Si}_8\text{O}_{11}(\text{OH})_2$, has been synthesized *via* a multi-step synthesis (52% yield). The structure was confirmed with ^{29}Si NMR, elemental analysis, and X-ray diffraction. X-ray diffraction revealed an incompletely-condensed structure that contains inter- and intramolecular hydrogen bonding between silanols. This structure is currently being functionalized to produce a wide variety of functional F-POSS based compounds and polymers.

INCOMPLETELY-CONDENSED FLUOROALKYL SILSESQUIOXANE: SYNTHESIS AND CRYSTAL STRUCTURE

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Introduction

Polyhedral oligomeric silsesquioxanes (POSS), an inorganic-organic hybrid material, has received attention as a class of robust nanometer-sized building blocks for the development of high performance materials.^{1,2} A recently developed sub-class of POSS, fluorinated polyhedral oligomeric silsesquioxane (F-POSS), consists of a Si-O core with a periphery of fluoroalkyl chains ranging from 6-12 carbon atoms in length.³ These compounds have proven to be useful in the creation of low-surface energy materials.^{4,5} Currently F-POSS is a standalone compound without any reactive chemical functionality. To circumvent the inert nature of these compounds, research has been performed on the functionalization of the (trifluoropropyl)₇Si₇O₉(OH)₃ with other long-chain fluorinated compounds to produce low surface energy materials.⁶ Although successful, this strategy was limited by the short length of the trifluoropropyl groups on the initial trisilanols. Herein, using a similar synthetic strategy to that developed by Feher and coworkers, we report a procedure to synthesize incompletely-condensed F-POSS.⁷ This work explains a detailed synthesis of the first incompletely-condensed fluoroalkyl silsesquioxane, (F-POSS-(OH))₂.

Experimental

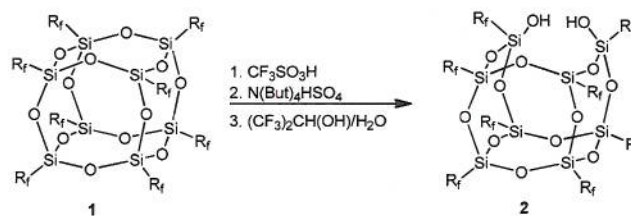
Materials. F-POSS (1) was synthesized using previously reported procedures. All reactions were performed under a nitrogen atmosphere unless otherwise noted.

Instrumentation. ¹H, ¹³C, and ²⁹Si NMR spectra were obtained on a Bruker 300-MHz or 400-MHz spectrometer. A heteronuclear inverse gated decoupling pulse sequence (NOE) with a 12 sec delay was used to acquire ²⁹Si NMR spectra. X-ray diffraction for compound 2 was collected at T=100.0 (K) using Kusing Bruker 3-circle, SMARTAPEX CCD with c-axis fixed at 54.748, running on SMART V 5.625 program (Bruker AXS: Madison, 2001). Graphite monochromated CuK α (λ = 1.54179 Å) radiation was employed for data collection and corrected for Lorentz and polarization effects using SAINT V 6.22 program (Bruker AXS: Madison, 2001), and reflection scaling (SADABS program, Bruker AXS: Madison, WI, 2001).

Synthesis of (CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₁(OH))₂ (2). Synthesis of compound 2 will be discussed in detail in future publication (53%). ²⁹Si{¹H} NMR (C₆F₆, 300 MHz) δ -59.2, -65.0, -68.2 (1:1:2). Anal. Calcd. for C₈₀H₃₄F₁₃₆O₁₃Si₈ (found): C, 23.94 (23.99), H, 0.85 (0.75), F, 64.44 (64.72).

Results and Discussion

Synthesis of (CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₁(OH))₂. A multi-step reaction procedure was developed to convert F-POSS (1) into an incompletely condensed silsesquioxane structure (2). The first step opened the cage with triflic acid to produce a ditriflate intermediate. This intermediate was reacted with tetrabutylammonium hydrogensulfate to produce another, more stable, bridged sulfate F-POSS intermediate. This sulfate compound was subsequently converted to the incompletely-condensed silsesquioxane (2) via a water and polar fluorinated solvent addition. The main side product from each of these steps is compound 1. ²⁹Si NMR, elemental analysis, and X-ray diffraction were used to confirm the structure of 2. The ²⁹Si NMR for compound 2 (-59.2, -65.0, -68.2) displayed a ²⁹Si chemical shift ratio of 1:1:2. The peak at -59.2 was attributed to the silanols on the POSS structure. This provided evidence for an open-caged structure.



1 (R_f = CH₂CH₂(CF₂)₇CF₃)

Scheme 1. Synthesis of disilanols F-POSS.

The crystal structure of compound 2 revealed an incompletely-condensed edge along the POSS cage (Figure 1). The long fluoroalkyl chains contained a large amount of positional and rotational disorder due to their flexibility. This made obtaining the crystal structure very difficult even at temperatures as low as 100K. The opened edge forms a dimeric structure with between two F-POSS cages via intermolecular hydrogen bonds between the silanol groups on adjacent cages. A dimeric hydrogen bonding contact is established from the intermolecular silanols at a distance of 2.798 Å and intramolecular silanols, O(1)···O(13) at a distance of 2.810 Å. This dimeric structure is thought to help stabilize the incompletely condensed structure.

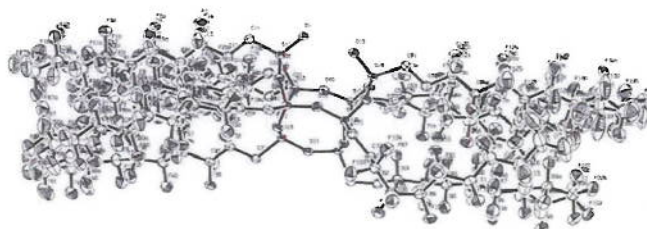


Figure 2. ORTEP of compound 2. Thermal ellipsoids are shown at 50% probability. Fluorinated chains contained substantial disorder.

Conclusions

The incompletely condensed fluoroalkyl silsesquioxane was successfully synthesized and characterized. This structure was further confirmed with X-ray diffraction. This structure is currently being functionalized to produce a wide variety of functionalized to produce a wide variety of functional F-POSS based compounds and polymers.

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References

- (1) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110*, 2081.
- (2) Li, G.; Wang, L.; Ni, H.; Jr., C. U. P. *J Inorg Organomet P* **2001**, *11*, 123.
- (3) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 4137.
- (4) Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544.
- (5) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H. *Adv. Mater.* **2009**, *21*, 2190.
- (6) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M. *Chem. Commun.* **2007**, 4992.
- (7) Feher, F. J.; Nguyen, F.; Soulivong, D.; Ziller, J. W. *Chem. Commun.* **1999**, 1705.